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Vibrational spectral studies on 2,5 dichloroaniline

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Abstract : Vibrational spectral studies on 2,5-dichloroaniline have been carried out. All the bands have been assigned on the basis of normal coordinate analysis which are in good agreement with the literature. The far IR region (20–600 cm^{-1}) has been investigated for the first time to pick up such fundamental frequencies which have not been reported so far. The laser Raman spectra of the molecules have been recorded in the region 100–4000 cm^{-1}.

Keywords : Vibrational spectra, Raman bands, normal coordinate analysis, 2,5 dichloroaniline

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1. Introduction

Vibrational spectral studies on benzene and mono-, di- and trisubstituted derivatives have attracted wide attentions [1–39]. However, complete assignments for all the vibrational modes have not been made. We have studied vibrational spectra of 2,5 dichloroaniline (Figure 1) and have assigned all the 39 vibrational modes for the first time.

2. Experimental

The compound 2,5-dichloroaniline was obtained from Koch-Light Laboratories Limited, England in solid state at room temperature. The compound was spectroscopically pure, hence no further purification was needed. The far infrared spectra were recorded on Fourier far I.R. spectrometer (model Polytec F I R 30) in the region 20–600 cm^{-1} (Figure 2). The spectra in this region were recorded by trapping the compound in the polyethylene matrix following the method described by Brash and Jakobsen [19]. The spectra were run at 2.5 cm^{-1} and 5 cm^{-1} resolutions in the regions 20–100 cm^{-1} and 100–600 cm^{-1} respectively.

The infrared spectra in solid phase with nujol mull and also in CCl_4 solution were recorded on Perkin Elmer (model 621) double beam grating spectrophotometer in the region 200–4000 cm^{-1} (Figure 3). The accuracy of measurements of the bands is estimated to be accurate within ±5 cm^{-1} in the region 200–2000 cm^{-1} and ±10 cm^{-1} in the region 2000–4000 cm^{-1} respectively. The Raman spectra (Figure 4) of these compounds were recorded in powder form on spex 1401 spectrophotometer consisting of argon-ion laser. The 5145 Å line of the Argon-ion laser was used to excite the Raman spectrum. The accuracy of measurement of the Raman bands is estimated to be accurate within ±5 cm^{-1}.

3. Results and Discussions

(a) Stretching vibrations :

In the present investigation all the three C-H stretching frequencies which are found to lie in the region 3000–3100 cm^{-1} have been observed (3085, 3060 and 3032 cm^{-1}) with week intensities in the infrared spectrum. The corresponding Raman bands have been observed at 3080, 3050 and 3055 cm^{-1}. The first two bands has been observed with weak intensities while the last one with strong intensity.

In substituted anilines the strong C-NH_2 vibration [12] appears near 1300 cm^{-1}. In the present case, the C-NH_2 stretching frequency has been observed at 1303 cm^{-1} with strong intensity in the infrared spectrum. The corresponding Raman band has been observed at 1308 cm^{-1} with weak intensity. The C-Cl stretching modes have

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been observed at 535 and 434 cm^{-1} with medium and strong intensities respectively in the infrared spectrum. Only one raman band corresponding to the same mode has been observed at 428 cm^{-1} with strong intensity. These assignments are in agreement with the assignments of previous workers [23,24] in the chlorine substituted benzenes.

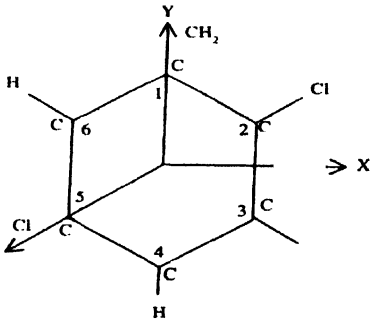

Figure 1. 2,5-Dichloroaniline

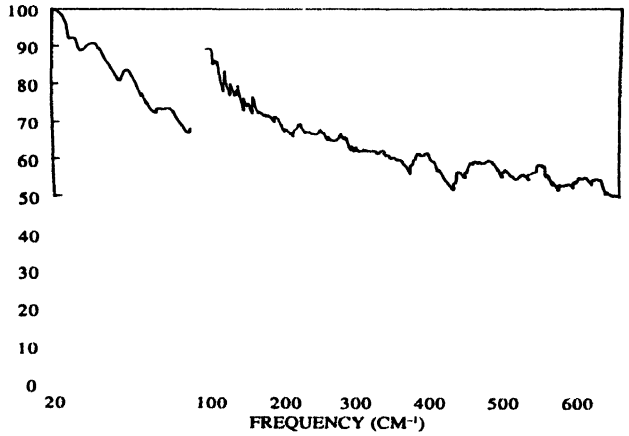

Figure 2. Far I.R spectra of 2,5-dichloroaniline.

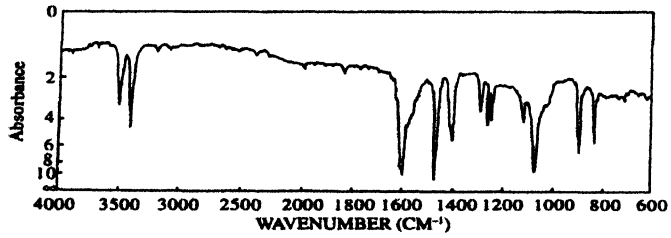

Figure 3. I.R spectra of 2,5-dichloroaniline.

The appearance of a group of six bands in the region 1000–1650 cm^{-1} in the spectra of substituted benzenes, represents the C-C stretching modes, represented by normal modes 8_a, 8_b, 19_a, 19_b, 14 and 1 in Wilson's notations.

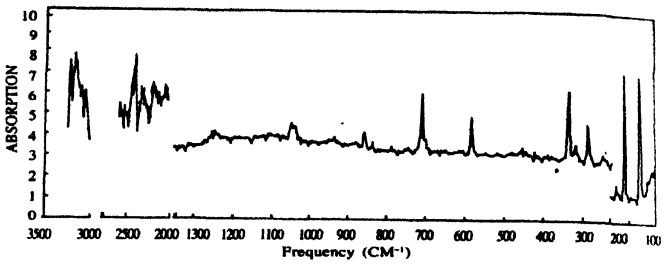

Figure 4. Raman spectra of 2,5-dichloroaniline.

Table 1. Fundamental frequencies (in cm^{-1}) of 2,5-dichloroaniline and their assignments.

Species	IR	Raman	Vibration number	Assignment
a'				
ν_1	3085(s)	3080(w)	2	$\nu_{(C-H)}$
ν_2	3060(m)	3050(w)	20_a	$\nu_{(C-H)}$
ν_3	3032(m)	–	20_b	$\nu_{(C-H)}$
ν_4	1608(s)	1609(w)	8_b	$\nu_{(C-C)}$
ν_5	1600(s)	1600(w)	8_a	$\nu_{(C-C)}$
ν_6	1482(s)	–	19_b	$\nu_{(C-C)}$
ν_7	1470(s)	–	19_a	$\nu_{(C-C)}$
ν_8	1303(m)	1308(w)	13	$\nu_{(C-NH_2)}$
ν_9	1290(m)	1278(m)	14	$\nu_{(C-C)}$
				Kekule vibration
ν_{10}	1268(m)	1268(w)	3	$\delta_{(C-H)}$
ν_{11}	1142(m)	–	18_b	$\delta_{(C-H)}$
ν_{12}	1086(s)*	1085(w)	15	$\delta_{(C-H)}$
ν_{13}	1048(s)*	1048(w)	1	$\nu_{(C-C)}$
				Ring breathing
ν_{14}	792(s)	790(w)	6_b	$\delta_{(C-C-C)}$
ν_{15}	733(w)	–	6_a	$\delta_{(C-C-C)}$
ν_{16}	535(m)	–	7_b	$\nu_{(C-Cl)}$
ν_{17}	505(m)	–	12	$\delta_{(C-C-C)}$
ν_{18}	434(s)	428(w)	7_a	$\nu_{(C-Cl)}$
ν_{19}	374(s)	–	18_a	$\delta_{(C-NH_2)}$
ν_{20}	270(m)	280(s)	9_b	$\delta_{(C-Cl)}$
ν_{21}	192(s)	188(s)	9_a	$\delta_{(C-Cl)}$
a''				
ν_{22}	932(m)	922(s)	17_b	$\gamma_{(C-H)}$
ν_{23}	898(s)	890(s)	5	$\gamma_{(C-H)}$
ν_{24}	832(s)	825(w)	11	$\gamma_{(C-H)}$
ν_{25}	718(m)	713(s)	4	$\gamma_{(C-C-C)}$
ν_{26}	575(s)	583(s)	16_a	$\gamma_{(C-C-C)}$
ν_{27}	448(s)	445(m)	16_b	$\gamma_{(C-C-C)}$
ν_{28}	205(m)	207(m)	10_a	$\gamma_{(C-NH_2)}$
ν_{29}	180(m)	188(s)	10_b	$\gamma_{(C-Cl)}$
ν_{30}	140(m)	145(m)	17_a	$\gamma_{(C-Cl)}$

* = These have been observed in CCl_4 solution; s = strong; ν = stretching; m = medium; δ = bending in plane; w = weak; γ = bending out of plane.

Except for the ring breathing vibration of benzene (normal mode 1) all these frequencies are known to remain practically unaffected by substitution. The bands observed in this region (except normal mode 1) have been assigned as corresponding to these modes in Table 2. The ring breathing mode in the present case has been assigned to the intense band at 1048 cm^{-1}. The corresponding Raman band has been observed at 1048 cm^{-1} with weak intensity.

Table 2. NH_2 frequencies (cm^{-1}) in 2,5-dichloroaniline and their assignments.

Species	I.R. Frequency (cm^{-1})	Assignment
ν_{31}	3485(s)	ν_{as} (NH_2)
ν_{32}	3405(s)	ν_s (NH_2)
ν_{33}	1645(m)	δ_s (NH_2) Scissoring
ν_{34}	1124(m)	ν_{as} (NH_2) Rocking
ν_{35}	620(s)	δ_{as} (NH_2) Wagging
ν_{36}	200(m)	γ(NH_2) Twisting

ν_{as} = asymmetric stretching; ν_s = symmetric stretching; δ_{as} = asymmetric in-plane-bending; δ_s = symmetric in-plane-bending; γ= out of plane bending.

Table 3. Combination and overtone NH_2 frequencies (cm^{-1}) in 2,5-dichloroaniline and their assignments.

IR Frequencies	Assignments
3508	3080 + 448 = 3508 (*A''*)
3395	3050 + 310 = 3395 (*A''*)
2930	1470 × 2 = 2940 (*A'*)
2860	1600 + 1265 = 2865 (*A'*)
2137	1265 + 932 = 2137 (*A''*)
1919	1086 + 832 = 1918 (*A'*)
1858	1280 + 575 = 1855 (*A''*)
1842	1048 + 792 = 1840 (*A'*)
1698	1265 + 434 = 1699 (*A'*)
1665	832 × 2 = 1664 (*A'*)
1370	832 + 535 = 1367 (*A'*)
1308	733 + 575 = 1308 (*A''*)
1268	753 + 535 = 1268 (*A'*)
1165	733 + 434 = 1167 (*A'*)
915	733 + 180 = 913 (*A''*)
830	448 × 2 = 896 (*A'*)
850	575 + 270 = 845 (*A''*)
765	575 + 192 = 767 (*A''*)
475	205 + 270 = 475 (*A''*)
372	180 + 192 = 372 (*A''*)
335	192 + 140 = 332 (*A''*)

(b) In-plane Bending Vibrations :

The C-H in plane bending vibrations represented by normal modes 3, 15 and 18_b are found to appear in the region [27,38] 1300–1100 cm^{-1} in the spectra of asymmetric trisubstituted benzenes. The three C-H in plane bending vibrations observed in the present investigation are well within the frequency interval given above.

Normal modes 9_a, 9_b and 18_a are regarded as the C-Cl in plane bending vibrations in the spectra of asymmetric trisubstituted benzenes. The two C-Cl in plane bending modes have been observed at 270 and 192 cm^{-1} with medium and strong intensities respectively in the infrared spectrum. The corresponding Raman bands have been observed at 280 and 188 cm^{-1} with strong intensities. These assignments are in agreement with the works of Rangacharyulu *et al* [29]. The C-NH_2 in plane bending mode represented by normal mode 18_a have been assigned at frequency of magnitude 374 cm^{-1} with strong intensity in the infrared spectrum. No Raman band corresponding to the same mode have been observed. This assignment finds support from the works of other workers [11,20] on similar and related molecules.

The C-C-C-C in plane bending vibrations are represented by normal modes 6_a, 6_b and 12. In the present investigation normal modes 6_b and 6_a have been assigned to frequencies of magnitudes 792 and 733 cm^{-1} in the infrared spectrum appearing with strong and weak intensities respectively. The Raman band corresponding to normal mode 6_b has been observed at 790 cm^{-1} with weak intensity. No Raman band has been observed corresponding to normal mode 6_a. Normal mode 12 is found to appear below the frequency of magnitude [29] 600 cm^{-1} in the spectra of trisubstituted benzenes with mixed substituents. In the present case the infrared band appearing at 505 cm^{-1} with strong intensity has been assigned to normal mode 12. No Raman band corresponding to the same mode has been observed.

(c) Out-of-plane bending vibrations :

As discussed in the case of 2,4-dichloroanilines, normal modes 17_b, 5 and 11 will be regarded as C-H out of plane bending vibrational modes in the present case. These modes are generally found to appear in the range 750–1000 cm^{-1} in the infrared spectra of substituted benzenes [22]. The positions of these C-H deformations are determined mainly by the relative position of the substituents [39]. The nature of the substituent is of almost no consequence. It is observed [38] that when the number of the adjacent hydrogen atoms on the ring is decreased, the out of plane C-H vibrations in general shows a further shift to higher magnitude. Making use of these as well as the frequency interval established by Varsanyi the frequencies 992, 898

and 832 cm^{-1} observed in the infrared spectrum have been assigned to normal modes 17_b, 5 and 11 respectively. The Raman bands corresponding to the same modes have been observed at frequencies 922, 890 and 825 cm^{-1} respectively. The Raman bands corresponding to normal modes 17_b and 5 have been observed with strong intensities while the band corresponding to normal mode 11 has been observed with weak intensity.

Normal modes 10_a, 10_b and 17_a are regarded as C-Cl out of plane deformation modes in the spectra of trisubstituted benzenes with mixed substituents [27]. In the present investigation these modes have been observed at frequencies 205, 180 and 140 cm^{-1} in the far infrared spectra. The first bands have been observed with medium intensities. The corresponding Raman bands have been observed at frequencies 207, 188 and 145 cm^{-1}. These assigned frequencies are well within the frequency intervals as established by Varsanyi [27] for the same modes.

The C-C-C ring deformation modes are represented by normal modes 4, 16_a and 16_b. In the present investigation the infrared frequency observed with medium intensity at 718 cm^{-1} has been assigned to normal mode 4. The corresponding Raman frequency has been observed at 713 cm^{-1} with strong intensity. Normal modes 16_a and 16_b has been observed at 575 and 448 cm^{-1} in the infrared spectrum with strong and medium intensities respectively. The corresponding Raman frequencies have been observed at frequencies of magnitudes 583 and 445 cm^{-1} with strong and medium intensities, respectively.

Internal vibrations of the NH_2 group :

The internal vibrations of the NH_2 group of the molecule 2,5-dichloroaniline have been given. The assignments have also been proposed. The N-H_2 stretching vibrations have been discussed in detail in the case of 2,4-dichloroaniline. In the present investigation the N-H asymmetric and symmetric stretching modes have been observed at frequencies 3485 and 3405 cm^{-1} appearing with strong intensities in the infrared spectrum. The scissoring and rocking modes have been observed at 1645 and 1124 cm^{-1} in the infrared spectrum with medium and strong intensities respectively. The wagging and twisting modes have been observed at 620 and 200 cm^{-1} with strong and medium intensities respectively.

Combination and overtone bands :

The combination and overtone bands observed in the infrared spectrum of 2,5-dichloroaniline have been analysed in Table 3. Most of these bands are of medium intensities.

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